Direct Observation of Reversible and Irreversible Oxidation of Layered J-Aggregate Supported above Au(111)

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Abstract

An Au(111) surface with a self-assembled cysteamine monolayer allows highly uniform two-dimensional (2D) J-aggregates of anionic cyanine dyes to be supported 10-15 angstroms above the Au(111) surface. This provides a superior model electrode system with which one can directly observe either reversible or irreversible oxidation of the 2D J-aggregate by the standard electrochemical method (cyclic voltammetry). Slow-scan voltammetry with scan rates less than ~1V/s invariably gave rise to an irreversible oxidation signal involving the interface charge transfer of overall 4 electrons/molecule. In contrast the reversible oxidation of the J-aggregate observed under the fast scan mode (10–100 V/s) represents a reversible charge transfer less than 1 electron/molecule between the HOMO levels of the J-aggregates and a continuum of electronic states of the gold electrode. Along with a series of voltammograms measured also for smaller J-aggregates with lower degrees of structural perfection, the results indicate that the oxidation potential of the J-aggregate is substantially more negative than that of the monomer. The J-aggregation of our test cyanine dye thus causes an upward shift of the HOMO level. It should be noted, however, that the effect of J-aggregation on the redox level critically depends on the nature of dye positive holes in the given aggregate framework.

Introduction

The J-aggregates of cyanine dyes, a common spectral sensitizer for silver halide photographic materials, are characterized by a sharp absorption that markedly red shifted from the monomer band. The energy gap between the dye HOMO and LUMO levels thus must be significantly narrowed by J-aggregation, but the absorption spectrum alone never tells us how this narrowing is correlated to the absolute shift in their energetic positions. The electrochemical potential data, available for a number of cyanine dyes but with respect to the monomers in solution, are likewise of little help in predicting the redox levels that are pertinent to the J-aggregate. This paper introduces our recent experimental approach to this long-standing issue, for which we made use of our recently developed method for controlled layering of two-dimensional (2D) J-aggregates of anionic cyanine dyes upon a self-assembled monolayer (SAM) of cysteamine (CA) on an atomically flat Au(111).[1] The CA SAM on gold provides a densely amino-group-functionalized surface, to which the J-aggregate monolayer of anionic cyanine dyes (with sulfonic acid end groups) can be successfully anchored via two ammonium sulfonate bonds on both sides of dye molecule. The resultant vertical geometry is as schematically illustrated in Figure 1 for a typical thiacarbocyanine dye (Dye 1) studied in this work.
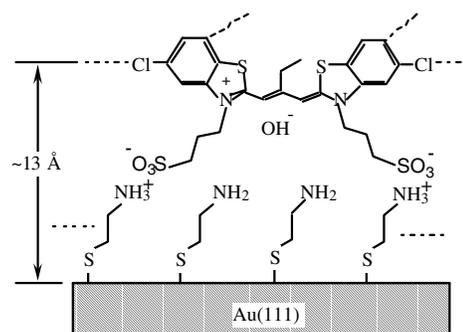

Figure 1 Cross-sectional view of 2D J-aggregate on CA/Au(111).

In the geometry of Figure 1, the J-aggregate monolayer is supported at a fixed distance, ~13 Å, above the Au(111) surface, and the interface electron transfer through this significant tunneling gap can be followed in situ under facile electrochemical control of the energetic position of the Dye HOMO level relative to the Fermi level of the gold electrode. The redox species (2D J-aggregate) here is firmly attached to the gold surface via the CA SAM, so that the entire assembly builds up a diffusionless electrode system in which the current-potential profiles obtained by the linear-sweep or cyclic voltammetry provide a straightforward

information about the interface electron transfer kinetics. Our samples thus serve as a superior model electrode system for directly investigating the redox properties of layered J-aggregates. The thiacarbocyanine dye we have studied is not at all special and readily undergoes an irreversible oxidation process as the majority of other cyanine dyes. Nonetheless, a considerably fast-scan voltammetry reaching 100 V/s at maximum allowed us to observe for the first time the reversible or quasi-reversible voltammograms for J-aggregates. We find that the J-aggregation in our model system, as opposed to what has been reported earlier by Lenhard and Hein,[2] causes a net negative (upward) shift in the oxidation potential (HOMO).

Experimental

In addition to the test cyanine dye, 5,5'-dichloro-3,3'-disulfopropyl-9-ethylthiacarbocyanine triethylamine (Dye 1) its thiacyanine analogue, 5,5'-dichloro-3,3'-disulfopropyl-9-ethylthiacyanine triethylamine (Dye 2), was used as an effective diluent, which by being coadsorbed with Dye 1 produces less-ordered Dye 1 J-aggregates with smaller domain sizes. The oxidation potential of Dye 2 is expected to be so positive that it is electrochemically inactive in the selected potential range. An atomically flat, high-quality Au(111) film, approximately 250 nm thick, was prepared on freshly cleaved natural mica by using the DC Ar-ion sputtering method as described elsewhere.[3] The self-assembled monolayer of CA was formed by immersing the Au(111) substrate in a 10 mM ethanolic solution of CA for ~5 min at room temperature (~20 °C), followed by rinsing with running ethanol. The dye adsorption onto the CA-covered Au(111) was allowed for typically 5 min at ~50 °C from a 0.1 mM dye solution.

All the electrochemical measurement was carried out at room temperature (~20 °C) in a three-electrode cell with a concentrated aqueous electrolyte (1.5 M KNO_3) solution. The working electrode potential was controlled with a scanning potentiostat in combination with an external function generator, relative to an Ag/AgCl/NaCl(3M) reference electrode. The counter electrode was a Pt wire 0.5 mm in diameter. The area of working electrode (the dye/CA-covered Au(111) film on mica) brought into contact with the electrolyte solution was adjusted to 4–30 mm^2 depending on the current level. The pH of the non-buttered KNO_3 solution was in the range of 6~7. The dissolved oxygen in the electrolyte was removed by N_2 gas bubbling before each experimental run.

Results and Discussion

Spectral Characterization of J-Aggregate Supported by CA SAM on Au(111)

With the CA-covered Au(111) a highest-quality 2D J-aggregate with an extraordinary sharp J-band forms preferentially on a densest but still not fully ordered CA

monolayer at a considerably high temperature (~50 °C) of dye adsorption.[1] This indicates that an interface structural tuning between the CA SAM and the overlying J-aggregate monolayer is of crucial importance. Spectrum *a* in Figure 2 represents such a sharp J-band (peaked at 657 nm) of Dye 1 J-aggregate prepared in this manner. Also included in Figure 2 are a series of absorption spectra measured for smaller and less perfectly ordered Dye 1 J-aggregates adsorbed from mixed dye solutions of Dye 1 and Dye 2 with various mixing ratios. The partition of Dye 1 J-aggregate by the coadsorbed diluent dye (Dye 2) caused systematic blue shift and peak broadening of Dye 1 J-band as expected. The vertical geometry of the Dye/CA/Au(111) interface was already shown in Figure 1. The 3,3'-disulfopropyl substituents, in cooperation with the CA monolayer, support the 2D J-aggregate monolayer at a fixed distance above the Au(111) surface. The exact distance depends on the presently unknown tilt angles of the supporting alkyl chains, but we roughly estimate it to be around ~13 Å.
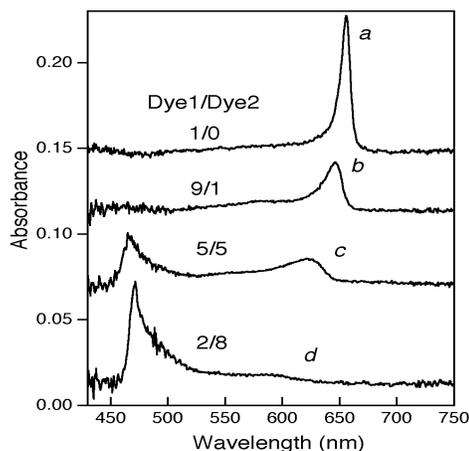
Figure 2 Absorption spectra of 2D J-aggregates of Dye 1 co-adsorbed in various mixing ratios with Dye 2 on CA/Au(111)
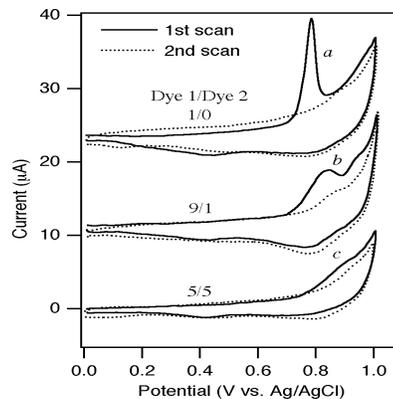
Figure 3 Slow-scan (25 mV/s) voltammograms of 2D J-aggregates of Dye with varied ratios with Dye 2.

Irreversible Oxidation under Slow-scan Mode

Figure 3 shows typical examples of slow-scan voltammograms obtained at scan rate of 25 mV/s for various J-aggregates of Dye 1 with and without the coadsorption of Dye 2 (the scan was always started at 0 V to the anodic direction). The highest-quality 2D J-aggregate with the sharpest J-band gives an exceptionally sharp oxidation peak at 0.79 V for the first anodic scan. The reverse scan gives no corresponding cathodic peak, indicating that the observed oxidation is totally irreversible. With increasing scan rate the position of this sharp anodic peak shifted from 0.76 V at 10 mV/s to 0.88 V at 1 V/s. The estimated integral current density under this anodic peak was 8.0×10^{-5} C/cm^2, or 5.0×10^{15} electrons/cm^2. Comparing this value with the absolute dye coverage at the saturation, 1.3×10^{14} molecules/cm^2 (measured by the ethanolic extraction method), we find that each dye molecule has given up a total of 4 electrons in the irreversible oxidation process. The resultant changes in the molecular structure are difficult to specify at present.

In Figure 3 the irreversible anodic peaks for the lower-quality Dye 1 J-aggregates coadsorbed with Dye 2 are strongly broadened. As mentioned later, however, the main cause of this broadening is not a probable increase in the site heterogeneity for such intentionally segmented J-aggregates. More importantly, a clear splitting of the anodic peak is visible in the middle voltammogram corresponding to Dye 1/Dye 2 mixing ratio of 9/1. The higher-potential sub peak is located at ~0.95 V, which is close to the reversible monomer oxidation potential (0.95-0.98 V) [4,5] reported for a cationic thiacarbocyanine dye with the same chromophore structure as that of Dye 1. An independent spectral evidence (not shown here) also proves that the above sub peak represents the irreversible oxidation of Dye 1 monomers isolated in the mixed aggregate framework. The fraction of isolated Dye 1 monomers increases with increasing mixing ratio of Dye 2, but the more serious broadening or flattening of the J-aggregate oxidation peak blurs out the monomer oxidation signal. Figure 3 thus indicates that the monomers are more difficult to oxidize than the J-aggregate. This agrees also with the reversible oxidation potential of the 2D J-aggregate and its domain-size dependence as discussed below.

Reversible Oxidation under Fast-scan Mode

With potential sweep rates well exceeding ~10 V/s a drastic change occurred in the form of cyclic voltammogram, so as to manifest a unique feature that reflects the reversible J-aggregate oxidation. Some examples obtained at the maximum scan rate of 100 V/s for the highest-quality J-aggregate are shown in Figure 4. In particular, when the switching potential (at which the scan direction was reversed from anodic to cathodic) was set at less than 0.95 V we obtained almost completely reproducible waves at least for the first several scans, accompanied by a well-defined cathodic peak at ~0.77 V with an estimated fwhm of 0.1–0.15 V. The integral current density under this cathodic peak was estimated to be at most

$\sim 2 \times 10^{-6}$ C/cm^2 or $\sim 1.5 \times 10^{13}$ electrons/cm^2, corresponding to roughly 10–15 % of a hypothetical one-electron oxidation of all dye molecules. The reversible feature that is best characterized by this cathodic peak was gradually weakened and finally lost with increasing switching potential, because potential is scanned over into the region where the irreversible oxidation easily sets in.
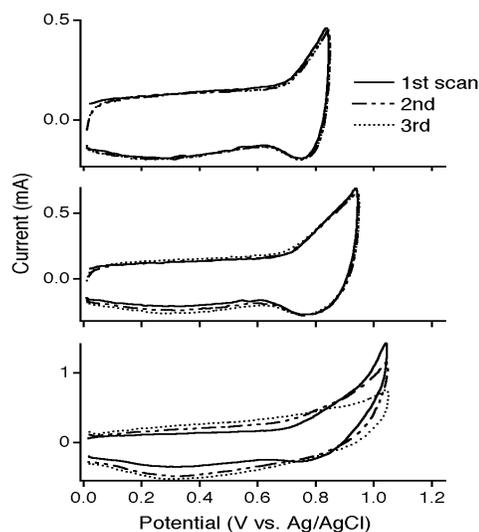

Figure 4 Fast-scan (100 V/s) voltammograms of highest-quality 2D J-aggregate of Dye 1 for some different switching potentials.
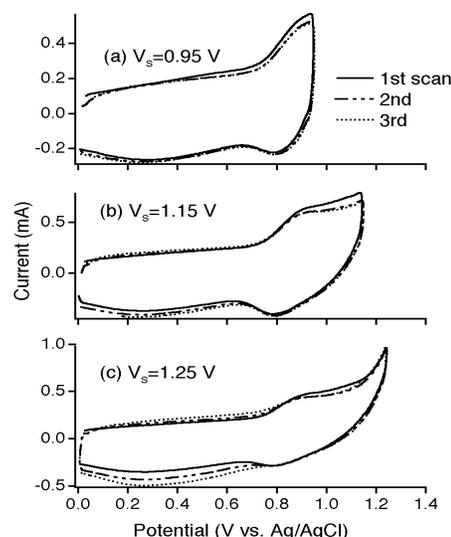

Figure 5 As Figure 4 but for a lower-quality J-aggregate of Dye 1 prepared at 5/5 mixing ratio with Dye 2.

Although the anodic scan does not give an obvious reversible peak in Figure 4, we do observe a shoulder-like oxidation signal which we expect would be peaked at ~0.83 V if the irreversible reaction were absent. The coupled anodic and cathodic signals then are separated for only ~60 mV from each other even at the maximum scan rate of 100

V/s. The reversible signals could be detected for scan rates down to 20 V/s, where the position of the anodic shoulder seemed almost coincided with the cathodic peak potential, which only slightly shifted to 0.78 V. We thus estimate the reversible oxidation potential of the highest-quality 2D J-aggregate to be 0.78 ± 0.01 V vs. Ag/AgCl.

Figure 5 shows typical fast-scan (100 V/s) voltammograms measured for a lower-quality 2D J-aggregate of Dye 1 prepared at 5/5 mixing ratio with Dye 2. The corresponding slow-scan voltammogram in Figure 3 shows an irreversible oxidation signal so flattened that it is hardly recognized as a definite anodic peak. In contrast the fast-scan voltammograms with a relatively low switching potential show reversible waves that are not much different from those for the highest-quality 2D J-aggregate, except that the cathodic peak noticeably shifted positively to ~0.8 V. More importantly, the shoulder-like anodic signal in Figure 4 is taken over by a distinguishable peak in Figure 5. Furthermore, it is only when the switching potential exceeded 1.3 V that the 0.8 V cathodic peak totally disappeared. These facts indicate that the irreversible oxidation sets in at more positive potentials for lower-quality J-aggregates. This naturally accounts also for the strong broadening of the irreversible anodic peak in the slow scan mode (Figure 3). If, there were any serious increase in the site heterogeneity for these smaller J-aggregates, the reversible redox peaks in the fast scan mode would also be broadened significantly. No such tendency can be discerned in Figure 5.

From the scan-rate dependence of the coupled reversible redox peaks in Figure 5, the reversible oxidation potential of the J-aggregate prepared at the 5/5 mixing level with Dye 2 was determined to be 0.82±0.01 V. In a like manner the reversible oxidation potential for the moderately high-quality Dye 1 J-aggregate prepared with a minor mixing of Dye 2 (9/1) was estimated to be 0.80±0.01 V, and that for the lowest-quality Dye 1 J-aggregate (at 2/8 mixing ratio) around ~0.85 V. Overall there is no doubt that the reversible oxidation potential shifts positively with decreasing aggregate size or quality. Furthermore the position of the irreversible monomer oxidation signal (0.93–1.0 V) in the slow scan conditions, which closely fit the reversible monomer oxidation potential (0.95–0.98 V) in solution, seems to be at a reasonable extreme position in the extension of the above potential order.

Once the ground-state reversible oxidation potential (HOMO level) is known, we can immediately deduce also the excited-state oxidation potential (LUMO level) using the experimental HOMO–LUMO transition energy. We then obtain the electronic energy diagram as shown in Figure 6. The systematic upward shift of the HOMO level by the J-aggregation is concomitant with the opposite (downward) shift in the LUMO level for the whole series of Dye 1 J-aggregates that considerably vary in domain size.

Energetics of Redox Level Shift

The upward shift of the HOMO level by J-aggregation indicates that a J-aggregate of Dye 1 carrying a dye positive

hole (oxidized form) acquires a substantially greater cohesive energy than in the absence of holes (reduced form). In other words the direction of shift in the HOMO level critically depends on how the dye positive holes are stabilized in the given aggregate framework in both static and dynamic sense. We presume that the hole in the 2D J-aggregate of Dye 1 may have a certain high mobility (if not as fast as exciton), though some experimental proof is necessary for this assumption. If on the contrary the holes were strongly localized, they would break up the otherwise homogeneous J-aggregate structure and thus negatively affect the cohesive energy. In this case it is only a static dielectric stabilization due to their excess positive charge that tends to lower the total energy of the oxidized form. This must be large enough to offset the above-noted structural disturbance for the observed shift in the HOMO level to be justified.
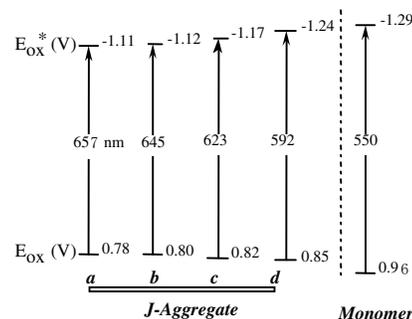
E_{OX}^* (V) — -1.11, -1.12, -1.17, -1.24, -1.29

657 nm, 645, 623, 592, 550

E_{OX} (V) — 0.78, 0.80, 0.82, 0.85, 0.96

a b c d

J-Aggregate   ***Monomer***

Figure 6 Energy level diagram for a series of J-aggregates derived from the experimental results.

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Biography

Mitsuo Kawasaki received his master degree of Engineering from Kyoto university in 1976 and a Doctor of Engineering from Kyoto University in 1985. He worked as a research instructor at the Industrial Chemistry Department of Kyoto University from 1976 to 1993, and made one-year visiting research at the University of California, Berkeley from 1988 to 1989. He moved to the Molecular Engineering Department of Kyoto University in 1993, and has been an Associate Professor of the same department since 1995. His current interest is in a variety of surface and interface phenomena, particularly those relating to the photographic processes in silver halides.